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Study of the Products of Pyrolysis Recycling. Sewage Sludge in the Aeration Station Almaty, Kazakhstan

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Abstract

This article presents the results of experimental studies of the process of pyrolysis recycling of sewage sludge aeration station in Almaty. According to experimental studies have provided the basic characteristics of the products of pyrolysis of sewage sludge disposal.

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Keywords: Ecology, waste water treatment plants, sewage sludge, pyrolysis, gas, liquid residue, the solid residue, net calorific value.

1. Introduction

The Republic of Kazakhstan, which is closely integrated into the world economy, has established one of its priorities the improvement of ecological environment for sustainable development. Environmental problem requires accelerated implementation of high-performance technologies to protect it.

In the process of mechanical and biological treatment of sewage at wastewater treatment plants are formed of various types sediments containing organic and mineral components [1,2,3].

Currently, sewage sludge in Kazakhstan mainly stored and kept on sludge drying beds, which has a negative impact on the environment [4].

Therefore, the solution treatment and disposal of sewage sludge is relevant, and the pyrolysis of sewage sludge is priority utilization in the context of Kazakhstan.

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Pyrolysis – the processing of carbonaceous materials by high-temperature heating without oxygen [5,6,7].

The pyrolysis reaction of organic deposits can be represented as follows [7,8,9]:

$$(C_6H_{10}0_5)_n \xrightarrow{i} nC_{x1}H_{y1}O_{z1}(\text{fuel gas}) + mC_{x2}H_{y2}O_{z2}(\text{resin}) + lC_{x3}H_{y3}O_{z3}(\text{the solid residue}) + kH_2O \quad (1)$$

Coming from the pyrolysis unit product is a complex mixture of gases, liquids and solids, the composition of which depends on the chemical nature of the raw materials and the physical parameters of heating.

Among mechanized methods of processing waste any preference should be given to the methods which allow not just eliminate and neutralize the waste, but make it possible to regenerate energy and materials and, of course, first and foremost their pyrolysis as a method that allows you to receive as a result of processing of commercial products [10].

Compared with the disposal of sludge by incineration technology for pyrolysis are less developed. However, in recent years scientists from different countries written many articles and reports on the pyrolysis of sewage sludge disposal. In the works of scholars have direct experimental methods for the study of the elementary processes in the pyrolysis, to identify the role of specific areas of the process [11-15].

2. Materials and methods

The purpose of the experimental study is to obtain a deeper understanding of the impact of different pyrolysis conditions (temperature and heating rate) on the basic characteristics of gas, liquid and solid fractions resulting from the pyrolysis of sewage sludge disposal and the question of the appropriateness of the technology pyrolysis recycling of sewage sludge, formed as a result of the technological cycle wastewater treatment aeration station Almaty, and subject to removal at the sludge beds.

As disposition of sewage sludge during the pilot study used a sample of sewage sludge aeration station prior to discharge Almaty on sludge beds. In accordance with the general rules of sampling was carried out manually. Prior to pyrolysis recycling sewage sludge was dehydrated and disinfected by heat treatment at a temperature of 110 0 C, where by the precipitate had a moisture content of 5.3% and an ash content of 30.0% and elemental composition (in terms of the organic substance): carbon – 47.7% nitrogen – 2.6% oxygen – 21.4%; hydrogen – 6.2%; sulfur – 1.2%. In order to obtain a more or less homogeneous fractions, the pellet was ground to a size less than 3 mm and sifted through a sieve, that is, when the pilot study unused pellet size 1-3 mm.

Experimental studies were carried out on the basis of the known schemes in the horizontal reactor [16]. Experimental studies were carried out in accordance with the relevant regulatory documentation, operating in Kazakhstan. The experimental setup is shown in Fig. 1.

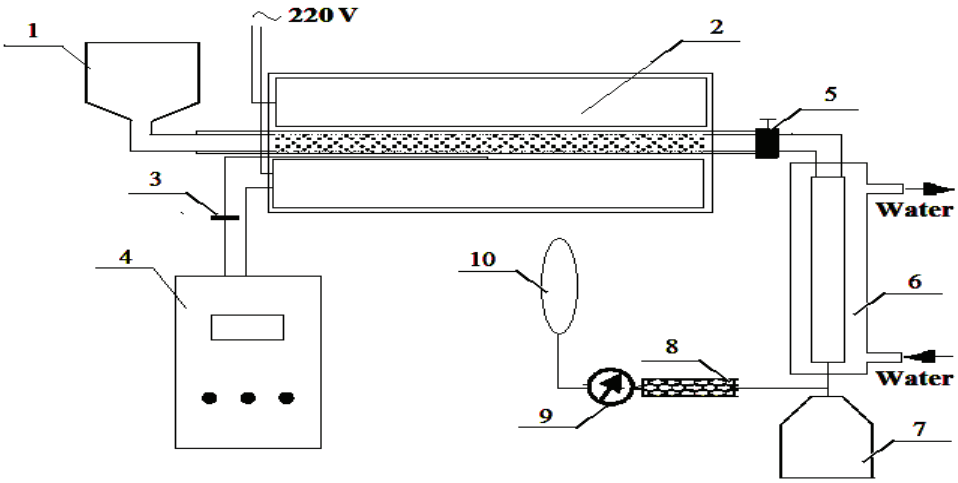

Fig. 1. Schematic of the experimental setup for pyrolysis

The experimental plant was operated as follows: initial sewage sludge in the amount of 1 kg/hr through funnel 1 fed to the pyrolysis reactor 2, where in the electric heater (5 kW) is heated to the required temperature (450, 650, 850 0C) at a heating rate of 5 and 50 °C per minute. The experimental setup equipped with a device 4 for controlling the temperature and thermocouple 3 to measure it. After treatment in the pyrolysis reactor, the liquid and gaseous mixture via the valve 5 to the cooler 6 directed, where cold water circulating through the cooling occurred. The gas temperature at the outlet of the reactor was 100-200 °C, respectively. Thereafter, the liquid 7 flowed to the tank, and the resulting pyrolysis gas fuel filtered through the filter with the load of the natural zeolite Chankanay field Kazakhstan, and then the purified gas is fed through a flow meter in the gas cylinder. The solid residue was unloaded after processing at the end of each test cycle. After that is weighted using the weights of laboratory-type models KERN 572-35 remaining weight of the solid residue.

Gas composition of the product gas mixture was determined experimentally using a portable gas analyzer IMR – 3000 gas chromatograph Agilent 7890B. Gas sampling for analysis performed by chromatography, is made directly from the plant after accounting for its amount by a flow meter. Hydrocarbons Ci – Cn dioxide and nitrogen are separated by gas-liquid chromatografhy, and the remaining components (hydrogen, oxygen, nitrogen), – gas-solid chromatographic method.

Study of the composition of liquid and solid samples is carried out by emission spectral analysis, atomic absorption spectrometry and photometry.

3. Results and discussion

The main objective was to analyze the actual composition of the resulting pyrolysis gas, liquid and solid fractions and the question of the appropriateness of the technology of pyrolysis of sewage sludge disposal for the development of complex technology of treatment and disposal of sewage sludge, taking into account the climatic conditions of the Republic of Kazakhstan.

The results of experimental analysis of the pyrolysis products studied productivity sludge disposal Almaty aeration station shown in Fig. 2 (at a heating rate of 50 °C per minute) and 3 (at a heating rate of 5 °C per minute).

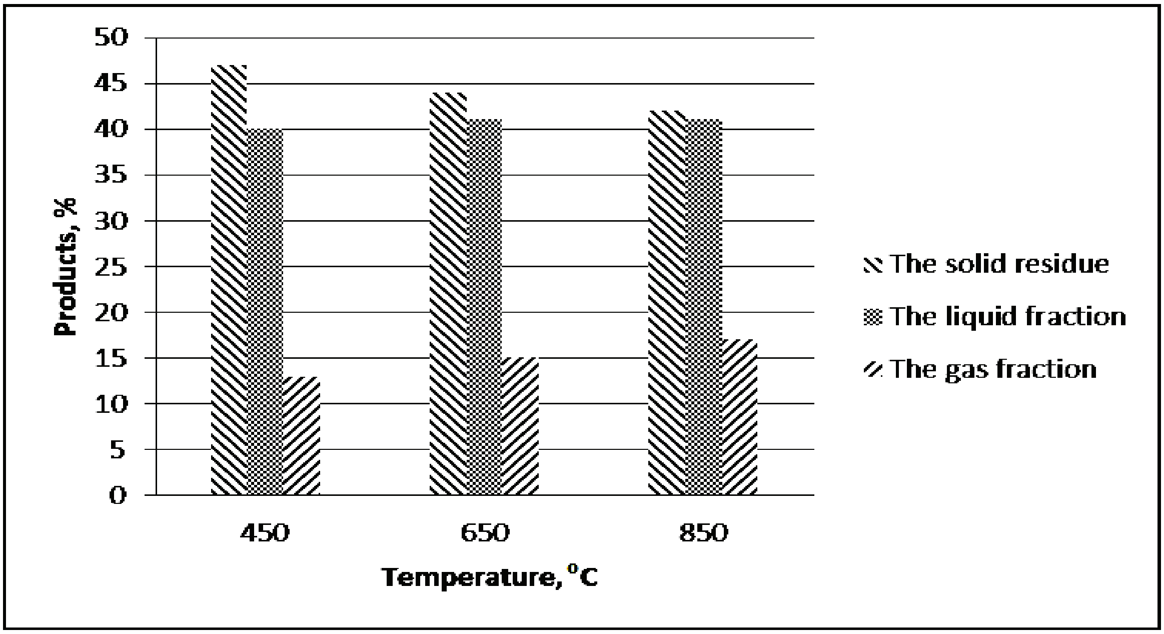

Fig. 2. The products of pyrolysis of sewage disposal water at a heating rate of 50 ° C per minute

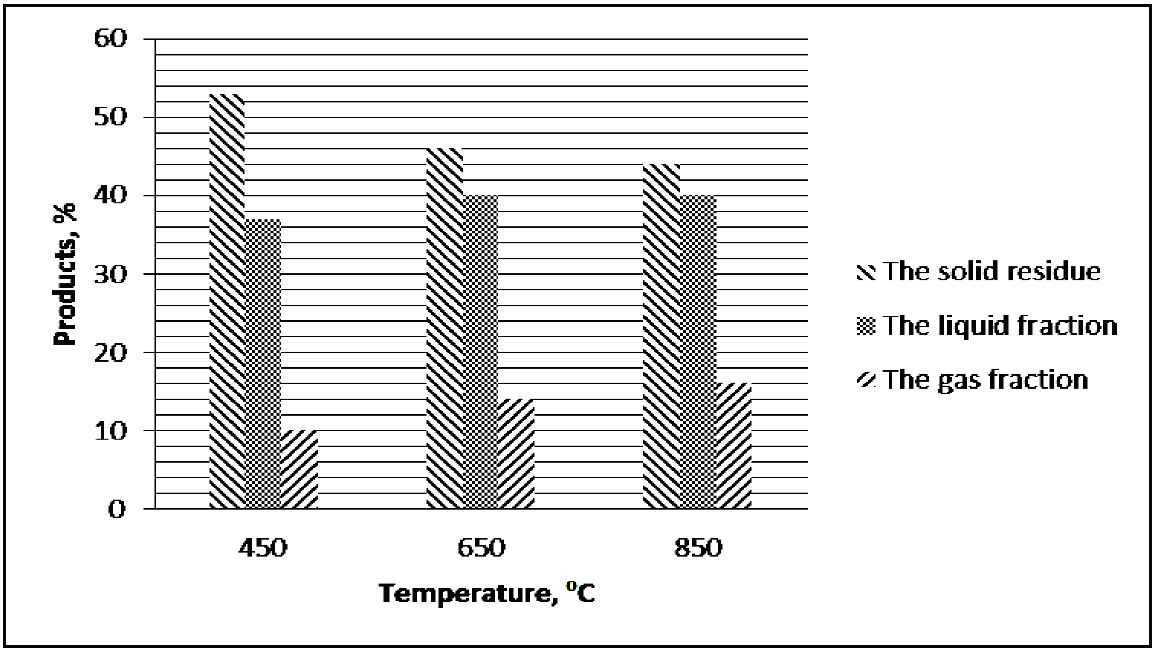

Fig. 3. The products of pyrolysis of sewage disposal water at a heating rate of 5 ° C per minute

From the above shown results show that productivity and chemical composition of the products of pyrolysis recycling depends on the operating conditions, that is, from the pyrolysis temperature and heating rate. As reported by other authors working with similar types of waste [16-19], the final pyrolysis temperature increase leads to a decrease of the solid residue and to increase the proportion of gas. The residue liquid increases somewhat when the heating temperature increases from 450 to 650 °C, but remains more or less constant at temperatures above 650 °C. The effect of the heating rate is only important at low heating temperatures, i.e. at 450 °C. Thus, at a temperature of 450 °C, the higher the heating rate, the more efficient utilization of pyrolysis, which leads to increased production of gases and liquids and solid reduction, and heating at a temperature above 650 °C, this effect is almost negligible.

Next, we studied the chemical composition of the investigated products of pyrolysis of sewage sludge disposal.

Analysis of the chemical composition of the gaseous waste products of pyrolysis has shown that CO2, CO, H2, O2, N2, and Hy,Cy are major components of the product gas. Some authors [18-22] noted that at lower temperatures, i.e. at 250-350 °C the main component of gas produced is CO2, while N2 is also present in small quantities. In this case, increasing the pyrolysis temperature leads to reduction of CO2, and to increase the CO and H2 in the entire temperature range. Hydrocarbons, CH4, C2H4, C2H6 and showed a maximum value at a temperature of 450 °C for C2H4 and C2H6, and at a temperature of 650 °C for CH4.

During the experimental studies have shown that at a heating rate of 50 °C per minute and 5 °C per minute gas formation is almost the same, it depends only on the temperature of the pyrolysis treatment of sewage sludge.

Tab. 1 shows the content of gaseous components depending on the temperature of pyrolysis of sewage sludge treatment at heating rates of 50 °C per minute and 5 °C per minute.

Table 1. Contents of gaseous components depending on the temperature of pyrolysis of sewage sludge treatment at heating rates of 50 ° C per minute and 5 ° C per minute

Name of the gaseous components	The content of gaseous components, [%]	
	At a heating rate of 50 [°C] per minute	At a heating rate of 5 [°C] per minute

	450 [°C]	650 [°C]	850 [°C]	450 [°C]	650 [°C]	850 [°C]
Oxygen (O2)	5.0	3.0	2.0	0.8	0.7	0.5
Carbon Monoxide (CO)	11.0	12.0	25.0	7.0	6.5	11.0
Nitrogen (N2)	22.0	10.0	11.0	4.0	5.0	7.0
Carbon dioxide (CO2)	11.0	4.0	2.0	20.0	2.5	0.5
Hydrogen sulfide (H2S)	0.003	0.001	0.000	0.000	0.000	0.000
Propane (C3H8)	0.006	0.008	0.008	0.01	0.01	0.009
Ethylene (C2H4)	3.0	2.0	1.0	2.0	0.5	0.01
Ethane (C2H6)	4.0	2.0	0.8	4.5	2.2	0.1
Methane (CH4)	16.0	26.0	8.0	22.0	17.0	9.0
Butane (C4H10)	0.04	0.01	0.01	0.05	0.02	0.01
Hydrogen (H2)	8.0	30.0	35.0	8.0	29.0	36.2

As seen from Tab. 1 the largest concentration in the gaseous products are hydrogen, carbon monoxide, methane, carbon dioxide and nitrogen. Next in descending order oxygen, ethane, propane, butane. Not found other possible products – ammonia (NH3), nitrogen oxides (NO, NO2). It should be noted that ammonia and nitrogen oxides – is environmentally harmful substances and the absence of a positive feature of this technology.

The highest content of hydrogen in a gas, as mentioned above, it is explained by the formation of sludges by the water gas shift reactions. Hydrogen gas could be much greater if part of it did not go on the formation of methane, ethane, propane, butane, pentane. Formation of carbon monoxide due to reaction of water gas. On a small content in the gas mixture of carbon dioxide can be assumed about the slow speed of the reaction of water gas, which is confirmed by the available data [17-22]. The content of other components in the product gas talks about the technical and environmental efficiency of these processes under these conditions.

The maximum value of the net calorific value of the resulting pyrolysis gas at a heating rate of 50 °C per minute is 16526.15 kJ/m3, which corresponds to a temperature of 650 °C. A heating rate of 5 °C per minute, the maximum value of the net calorific value of the pyrolysis gas is obtained 13736.966 kJ/m3, which corresponds to a temperature of 450 °C. This suggests that to achieve the desired amount of pyrolysis gas sufficient heating to a temperature of 650 °C at a heating rate of 50 °C per minute to a temperature of 450 °C at a heating rate of 5 °C per minute. In addition, at a temperature of 450 °C and a heating rate of 5 °C per minute to obtain the maximum amount of carbon dioxide (CO2) that characterizes a sufficiently high speed of the water gas shift reaction.

The liquid after the pyrolysis treatment of sewage sludge was a dark brown organic liquid having a water content. The obtained liquid fraction from the pyrolysis of sewage sludge is very easily divided into two layers: the top oily, curable at room temperature and the bottom layer a heavier pyroligneous (pyrogenetic) water.

In this case, the content of water in the pyroligneous averaged 30-40% of the resulting liquid. The second component of the liquid fraction of the pyrolysis products is the primary pitch (resin), the greatest interest to us is the product. Tab. 2 shows the chemical composition of the obtained liquid fraction of the second component.

Table 2. Chemical composition of the second component of the liquid fraction (primary tar)

Name of chemical elements	The content of chemical elements, [%]					
	At a heating rate of 50 [°C] per minute			At a heating rate of 5 [°C] per minute		
	450 [°C]	650 [°C]	850 [°C]	450 [°C]	650 [°C]	850 [°C]
Carbon (C)	61.7	49.1	55.8	62.7	56.1	56.7
Hydrogen (H)	10.75	10.2	9.8	11.5	10.3	10.1
Nitrogen (N)	5.75	5.2	5.5	5.2	5.2	5.2
Oxygen (O)	21.2	34.8	28.5	20.4	28.2	27.8
Sulfur (S)	0.56	0.43	0.45	0.44	0.44	0.44

The maximum value of the net calorific value obtained a second component of the liquid fraction (primary tar) at a heating rate of 50 °C per minute is 20607.433 kJ/m3 , which corresponds to a temperature of 450 °C. A heating rate of 5 °C per minute, the maximum value NCV obtained liquid fraction of the second component (primary tar) of 21744.11 kJ/m3, which also corresponds to a temperature of 450 °C. This suggests that to achieve the desired amount of fluid to a temperature sufficient heating at 450 °C heating rate 50 °C and 5 °C per minute.

After pyrolysis recycling of sewage sludge in the reactor remained solid, which presented a black dispersed in the powder mass. Chemical composition and characteristics of the solid residue are shown in Tab. 3.

Table 3. Chemical composition and characteristics of the solid residue

Names of Parts	Component Contents, [%]					
	At a heating rate of 50 [°C] per minute			At a heating rate of 5 [°C] per minute		
	450 [°C]	650 [°C]	850 [°C]	450 [°C]	650 [°C]	850 [°C]
Humidity	0.5	1.1	1.1	0.9	0.8	1.4
Ash content	58.0	62.4	66.3	51.7	60.3	62.3
Volatile matter	18.4	11.0	5.7	23.1	11.9	4.6
pH	8.2	8.6	11.9	8.0	9.0	11.7
Carbon (C)	32.9	32.2	32.6	38.0	33.8	36.4
Hydrogen (H)	2.0	1.4	0.9	2.7	1.4	0.9
Nitrogen (N)	2.4	2.0	1.2	2.6	2.5	1.3
Oxygen (O)	6.5	4.1	1.5	6.4	4.2	1.7
Sulfur (S)	0.62	0.6	0.56	0.63	0.63	0.64

The maximum value net calorific value of the resulting solid residue waste pyrolysis at a heating rate of 50 °C per minute is 8695.218 kJ/m3, which corresponds to a temperature of 450 °C. A heating rate of 5 °C per minute, the maximum value of the net calorific value of the resulting solid residue is waste pyrolysis 10567.087 kJ/m3, which also corresponds to a temperature of 450 °C. Compared with liquid and gaseous products obtained during this pyrolysis recycling waste pyrolysis solid residue has a lower heat of combustion less.

In this case, the residual content of the organic part of the solid pyrolysis residue disposal no more than 2.0–2.5%. This can be attributed to a deeper level of processing carbon component due to the use of high-temperature pyrolysis technology utilization of precipitation that allows you to change the volume ratio of the pyrolysis products in the direction of increasing separation of the gas phase by reducing the formation of the solid and liquid fractions. This gives, in turn, possible to avoid further processing of complex technologies and coal sludge directly use the combustible gas (after cleaning).

On the other hand the high ash content of the final product, i.e. solid waste pyrolysis, which is 51.7-66.3%, can be explained by the properties of recyclable rainfall as low concentrations of organic components, which should also help improve the degree of processing of carbon.

Due to the low content of organic fraction that is due to the lower net calorific value, in contrast to liquid and gaseous products obtained by pyrolysis of the waste, the use of the resulting solid residue as fuel techno-economically unfeasible.

4. Conclusions

According to the results of experimental studies the following conclusions can be drawn:

- As a result of experimental studies found that the utilization efficiency of the pyrolysis temperature is dependent on the rate of heating and pyrolysis. The residue liquid increases somewhat when the heating temperature increases from 450 to 650 °C, but remains more or less constant at temperatures above 650 °C. The effect of the heating rate is only important at low heating temperatures, i.e. at 450 °C. At a temperature of 450 °C, the higher the heating rate, the more efficient utilization of pyrolysis, which leads to increased production of gases and liquids and solid reduction, and heating at a temperature above 650 °C, this effect is almost negligible;

- The results of experimental studies have shown that at a heating rate of 50 ° C per minute and 5 °C per minute gas formation is almost the same, it depends only on the temperature of the pyrolysis treatment of sewage sludge, thus increasing the pyrolysis temperature led to a reduction in CO2, and an increase in CO and H2 in the whole temperature range. Hydrocarbons, CH4, C2H4, C2H6 and showed a maximum value at a temperature of 450 °C for C2H4 and C2H6, and at a temperature of 650 °C for CH4. To obtain the necessary amount of the pyrolysis gas is sufficient heating to a temperature of 650 °C at a heating rate of 50 °C per minute to a temperature of 450 °C at a heating rate of 5 °C per minute;
- The results of experimental studies revealed that the resulting liquid fraction is very easily divided into two layers: the top oily, and the bottom layer of heavier pyroligneous water. To obtain the necessary amount of liquid sufficient heating to a temperature of 450 ° C at a heating rate of 50 ° C and 5 ° C per minute;
- After pyrolysis recycling of sewage sludge in the reactor remained solid residue contains the chemical composition,%: carbon (C) -32.2-38.0; hydrogen (H) – 0.9-2.7; Nitrogen (N) – 1.2-2.6; Oxygen (O) -1.5-6.5; Sulfur (S) – 0.56-0.64. Maximum net calorific value of the solid residue obtained at a heating rate of 50 °C per minute is 8695.218 kJ/m3, which corresponds to a temperature of 450 °C. A heating rate of 5 °C per minute is 10567.087 kJ/m3, which also corresponds to a temperature of 450 °C. According to the results of experimental studies proved that the use of the resulting solid residue as fuel inappropriate.

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